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Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

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<b>UTILITY PATENT APPLICATION TRANSMITTAL</b> <small>(Only for new nonprovisional applications under 37 CFR 1.53(b))</small>		Attorney Docket No. <b>TI-25250</b>	
		First Named Inventor or Application Identifier <b>Patricia Smith</b>	
		Title <b>HYDROGEN PLASMA PHOTORESISTANT STRIP AND POLYMERIC RESIDUE CLEANUP PROCESS OXYGEN-SENSITIVE MATERIALS</b>	
		Express Mail Label No. <b>EL071337140US</b>	

<b>APPLICATION ELEMENTS</b> <small>See MPEP Chapter 600 concerning utility patent application contents</small>		<b>ADDRESS TO:</b> Assistant Commissioner for Patents Box Patent Application Washington, DC 20231	
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1. <input checked="" type="checkbox"/> Fee Transmittal Form (e.g., PTO/SB/17) <small>(Submit an original, and a duplicate for fee processing)</small>	6. <input type="checkbox"/> Microfiche Computer Program (Appendix)
2. <input checked="" type="checkbox"/> Specification (preferred arrangement set forth below) [Total Pages <b>22</b> ] - Descriptive title of the Invention - Cross References to Related Applications - Statement Regarding Fed sponsored R&D - Reference to Microfiche Appendix - Background of the Invention - Brief Summary of the Invention - Brief Description of the Drawings (if filed) - Detailed Description - Claim(s) - Abstract of the Disclosure	7. Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary) a. <input type="checkbox"/> Computer Readable Copy b. <input type="checkbox"/> Paper Copy (identical to computer copy) c. <input type="checkbox"/> Statement verifying identical of above copies
3. <input checked="" type="checkbox"/> Drawing(s) (35 USC d113) [Total Sheets <b>9</b> ] 4. Oath or Declaration [Total Pages <b>1</b> ] a. <input checked="" type="checkbox"/> Newly Executed (original or copy) b. <input type="checkbox"/> Copy from a prior application (37 CFR §1.63(d)) <small>(for continuation/divisional with Box 17 completed)</small> <b>[Note Box 5 below]</b> <b>DELETION OF INVENTOR(S)</b> i. <input type="checkbox"/> Signed statement attached deleting inventor(s) named in the prior application, see 37 CFR §1.63(d)(2) and 1.33(b).	
5. <input type="checkbox"/> Incorporation By Reference (useable if Box 4b is checked) The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.	

<b>ACCOMPANYING APPLICATION PARTS</b>	
8. <input checked="" type="checkbox"/> Assignment Papers (cover sheet & Documents(s)) 9. <input checked="" type="checkbox"/> 37 CFR §3.73(b) Statement (when there is an assignee) <input checked="" type="checkbox"/> Power of Attorney 10. <input type="checkbox"/> English Translation Document (if applicable) 11. <input type="checkbox"/> Information Disclosure Statement (IDS)/PTO-1449 <input type="checkbox"/> Copies of IDS Citations 12. <input type="checkbox"/> Preliminary Amendment 13. <input checked="" type="checkbox"/> Return Receipt Postcard (MPEP 503) (Should be specifically itemized) 14. <input type="checkbox"/> Small Entity Statement(s) <input type="checkbox"/> Statement filed in prior application Status still proper and desired (PTO/SB/09-12) 15. <input type="checkbox"/> Certified Copy of Priority Document(s) if foreign priority is claimed 16. <input type="checkbox"/> Other	

\*A new statement is required to be entitled to pay small entity fees, except where one has been filed in a prior application and is being relied upon

**17. If a CONTINUING APPLICATION, check appropriate box and supply the requisite information below and in a preliminary amendment:**

☐ Continuation   
 ☐ Divisional   
 ☐ Continuation-in-part (CIP)   
 of prior application No: /

Prior application information: Examiner \_\_\_\_\_ Group / Art Unit: \_\_\_\_\_

**18. CORRESPONDENCE ADDRESS**

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Signature	<i>Mark A. Valetti</i>	Date	<b>11/25/98</b>

**FEE TRANSMITTAL**

Patent fees are subject to annual revision on October 1.  
 These are the fees effective October 1, 1997.  
 Small Entity payments must be supported by a small entity statement,  
 otherwise large entity fees must be paid. See Forms PTO/SB/09-12.

**Complete If Known**

Application Number  
 Filing Date **11/26/97**  
 First Named Inventor **Patricia Smith**  
 Examiner Name  
 Group / Art Unit  
 Attorney Docket No. **TI-25250**

TOTAL AMOUNT OF PAYMENT (\$ **878**)

**METHOD OF PAYMENT**

1. ☒ The Commissioner is hereby authorized to charge to the following Deposit Account,

Deposit Account Number

**20-0668**

Deposit Account Name

**Texas Instruments Incorporated**

- ☒ Charge any additional fee required or credit any overpayment ☐ Charge all indicated fees and any additional fee required or credit any overpayment

2. ☐ **Payment Enclosed:**

☐ Check ☐ Money Order ☐ Other

**FEE CALCULATION****1. BASIC FILING FEE**

Large Fee Code	Entity Fee (\$)	Small Fee Code	Entity Fee (\$)	Fee Description	Fee Paid
101	790	201	395	Utility filing fee	<b>\$790</b>
106	330	206	165	Design filing fee	\$
107	540	207	270	Plant filing fee	\$
108	790	208	395	Reissue filing fee	\$
114	150	214	75	Provisional filing fee	\$

SUBTOTAL (1) (\$ **790**)

**2. EXTRA CLAIM FEES**

	Extra Claims	Fee from below	Fee Paid
Total Claims <b>24</b>	-20** = <b>4</b>	<b>22</b>	<b>88</b>
Independent Claims <b>3</b>	-3** = <b>0</b>	<b>82</b>	<b>0</b>
Multiple Dependent		<b>270</b>	<b>0</b>

\*\*or number previously paid, if greater; For Reissue, see below

Large Fee Code	Entity Fee (\$)	Small Fee Code	Entity Fee (\$)	Fee Description
103	22	203	11	Claims in excess of 20
102	82	202	41	Independent Claims in excess of 3
104	270	204	135	Multiple dependent claims in excess of 3
109	82	209	41	**Reissue independent claims over original patent
110	22	210	11	**Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) (\$ **88**)

**FEE CALCULATION (continued)****3. ADDITIONAL FEES**

Large Fee Code	Entity Fee (\$)	Small Fee Code	Entity Fee (\$)	Fee Description	Fee Paid
105	130	205	65	Surcharge - late filing fee	
127	50	227	25	Surcharge - late provisional filing fee or cover sheet	
139	130	139	130	Non-English specification	
147	2,520	147	2,520	For filing a request for reexamination	
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	
115	110	215	55	Extension for reply within first month	
116	400	216	200	Extension of time within second month	
117	950	217	475	Extension of time within third month	
118	1,510	218	755	Extension of time within fourth month	
128	2,060	228	1,030	Extension of time within fifth month	
119	310	219	155	Notice of Appeal	
120	310	220	155	Filing a brief in support of an appeal	
121	270	221	135	Request for oral hearing	
138	1,510	138	1,510	Petition to institute a public use proceeding	
140	110	240	55	Petition to revive - unavoidable	
141	1,320	241	660	Petition to revive - unintentional	
142	1,320	242	660	Utility issue fee (or reissue)	
143	450	243	225	Design issue fee	
144	670	244	335	Plant issue fee	
122	130	122	130	Petitions to the Commissioner	
123	50	123	50	Petitions related to provisional applications	

Other fee (specify) \_\_\_\_\_

Other fee (specify) \_\_\_\_\_

\*Reduced by Basic Filing Fee Paid

SUBTOTAL (3)

**SUBMITTED BY**

Typed or Printed Name

**Mark A. Valetti**

Signature

*Mark A. Valetti*

Date

**11/25/98**

Complete (if applicable)

Reg. Number

**36,707**

Deposit Account User ID

# HYDROGEN PLASMA PHOTORESIST STRIP AND POLYMERIC RESIDUE CLEANUP PROCESS FOR OXYGEN-SENSITIVE MATERIALS

## CROSS-REFERENCE TO RELATED PATENT/PATENT APPLICATIONS

The following commonly assigned patent/patent applications are hereby incorporated herein by reference:

Patent No./Serial No.

Filing Date

TI Case No.

TI-26189

## FIELD OF THE INVENTION

The instant invention pertains to semiconductor device fabrication and processing and more specifically to post metal pattern and etch clean-up processing.

## BACKGROUND OF THE INVENTION

Most semiconductor devices utilize several different levels of metallization. With the increasing complexity of devices and the need to reduce the physical size of devices, the number of levels which incorporate metal connections is increasing. In addition, with the desire to increase the speed of the devices while reducing the power consumed by the devices, advanced metallization schemes are being developed. One such scheme involves the use of copper-doped aluminum or copper structures for the bus lines and interconnects. Additionally, interlevel dielectrics with lower dielectric constants than standard silicon dioxide films may be used as the dielectric material situated between metallic structures.

A problem that most semiconductor manufacturers face is the cleaning up of the metallic structures after the structures are patterned and etched. More specifically, the photoresist needs to be removed, and the residual metal halide etch byproducts have to be removed or converted to different chemical forms to avoid corrosion of the metal. These processes, commonly known as strip and passivation processes, may cause non-conducting residues to form on the metallic structure. In order to address this problem, a cleaning step is typically performed after the metal structure is exposed and the photoresist is removed. The cleanup step will preferably remove all of the residue, typically comprised of inorganic polymers, that are formed on the metal structure, thus inhibiting corrosion of the metal structures. However, the clean step must not appreciably affect the electrical critical dimension (CD) of the metal structure.

Typically, for a metallization scheme consisting primarily of Al, the cleanup process consists of an HF vapor etch and an optional solvent clean. More specifically, an O<sub>2</sub>/H<sub>2</sub>O plasma photoresist strip and metal passivation step is performed followed by an *ex situ* HF vapor etch and solvent cleanup. The use of the separate HF vapor treatment equipment and the subsequent solvent "wet" clean increases processing costs and reduces production throughput. The use of a solvent is additionally undesirable due to environmental issues. Solvent recycling further increases the cost of the traditional cleanup process. In addition, both the HF vapor and solvent clean can cause CD loss, and may undercut the TiN/Ti barrier layers between the conductor and the dielectric substrate. Such cleanup processes may not sufficiently passivate the aluminum conductors, thereby resulting in the corrosion of the structure. Hence, a dry process which is environmentally friendly and which passivates the metal structure would be preferable. The use of an O<sub>2</sub>/H<sub>2</sub>O plasma passivation and strip step to remove the photoresist followed by an *in situ* O<sub>2</sub>/CF<sub>4</sub> or H<sub>2</sub>O/CF<sub>4</sub> plasma clean step to remove the polymeric residue from the metal structure has been used. However, the fluorine plasma may erode the process equipment in which this step is performed (*e.g.* any quartz parts in the process chamber would be eroded by the fluorine containing plasma).

For a typical Cu metallization scheme, a standard O<sub>2</sub> plasma ash is performed to remove photoresist after a via etch process. Since ashing with O<sub>2</sub> causes substantial oxidation to any exposed Cu at the bottom of the via, the via etch process generally completes to the Si<sub>3</sub>N<sub>4</sub> barrier layer typically deposited to prevent Cu oxidation. The nitride layer must then be removed in a separate wet or dry etch process. Thus, a dry plasma etch process which could be used to remove photoresist without oxidation of Cu would simplify the process flow by either eliminating the need for the Si<sub>3</sub>N<sub>4</sub> barrier layer, or substantially thinning it (it might still be useful as an etch stop layer for via formation). Removal or thinning of the Si<sub>3</sub>N<sub>4</sub> barrier layer would ease the oxide etch selectivity requirements since stopping the etch on the Si<sub>3</sub>N<sub>4</sub> layer would not be necessary.

## SUMMARY OF THE INVENTION

An embodiment of the instant invention is a hydrogen-containing plasma processing step to be used after the metal structure is etched. This novel step will passivate most metal structures, remove the polymeric residue from the sidewalls of the metal structures, and will remove the photoresist. In addition, this novel step has the following advantages over the prior art methods: it is a higher throughput process, it can be done in situ in any resist strip equipment regardless of the plasma energy source (e.g. a downstream microwave plasma source or a conventional RF plasma source), it provides better passivation of the exposed metal pattern by converting the metal halide residues into volatile hydrogen halides, it does not substantially oxidize the exposed Cu and therefore may be used in structures without Cu-barrier layers present, it does not produce hazardous waste, and it does not corrode the processing equipment.

An embodiment of the instant invention is a method of fabricating an electronic device formed on a semiconductor wafer, the method comprising the steps of: forming a layer of a first material over the substrate, the first material is oxygen-sensitive; forming a photoresist layer over the layer of the first material; patterning the layer of the first material; removing the photoresist layer after patterning the layer of the first material; and subjecting the semiconductor wafer to a plasma which incorporates a gas which includes hydrogen or deuterium so as to remove residue from the first material.

Preferably, the step of removing the photoresist layer is performed by subjecting the semiconductor wafer to the plasma which incorporates a gas which includes hydrogen or deuterium; or it is performed by subjecting the semiconductor wafer to a higher temperature step which is conducted in a hydrogen ambient with a plasma impinging upon the semiconductor wafer. The higher temperature is, preferably, around 245 °C.

In an alternative embodiment, the gas additionally includes a forming gas. Preferably, the forming gas is comprised of a gas consisting of: argon, nitrogen, and any other inert gas.

Preferably, the first material is comprised of a conductive material. More specifically, the first material is, preferably, comprised of: copper, tantalum, titanium, titanium nitride, tungsten, tungsten nitride, aluminum, copper-doped aluminum, silver, gold, and any combination thereof.

Another embodiment of the instant invention is a method of forming a conductive feature comprised of an oxygen-sensitive material over a semiconductor substrate for an electronic device, the method comprising the steps of: forming a conductive layer over the semiconductor substrate, the conductive layer comprised of the oxygen-sensitive material; forming a photoresist layer over the conductive layer, the photoresist having a pattern so as to expose portions of the conductive layer; removing the exposed portions of the conductive layer so as to form the conductive structure; and subjecting the semiconductor wafer to a plasma which incorporates a gas which includes hydrogen or deuterium. Preferably, the oxygen-sensitive material is comprised of copper, tungsten, tungsten nitride, tantalum, titanium, TiN, aluminum, copper-doped aluminum, silver, or gold.

Another embodiment of the instant invention is a method of fabricating a conductive interconnect for providing an electrical connection between a first conductor and a second conductor for an electrical device formed in a semiconductor substrate, the method comprising the steps of: forming a dielectric layer on the first conductor, the dielectric layer having at least one opening which exposes the first conductor; forming a layer of an oxygen-sensitive material on the dielectric layer, the oxygen-sensitive material substantially filling the opening in the dielectric layer and for providing an electrical contact to the first conductor; forming a photoresist layer on the oxygen-sensitive material, the photoresist layer having a pattern so as to expose portions of the oxygen-sensitive material; removing the exposed portions of the oxygen-sensitive material on the dielectric material, the removal step causing a residue to be formed on exposed surfaces of the remaining portions of the oxygen-sensitive

material; and removing the photoresist layer by subjecting the photoresist layer with a hydrogen-containing gas incorporated into a plasma. Preferably, the oxygen-sensitive material is comprised of a material selected from the group consisting of: copper, tungsten, tungsten nitride, tantalum, titanium, titanium nitride, aluminum, copper-doped aluminum, silver, gold, and any combination thereof. This embodiment of the instant invention may further comprising the step of: removing the residue by subjecting the residue to a fluorinated etchant, where the fluorinated etchant is, preferably comprised of  $\text{CF}_4$  or  $\text{CHF}_3$ .



## BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a flow diagram illustrating the method of one embodiment of the instant invention. This method is preferably utilized in a damascene process flow where oxygen-sensitive (metal) structures are exposed (during the via etch process, preferably).

FIGUREs 2a-2e are cross-sectional views of a semiconductor device which is fabricated using the method of the instant invention (which is illustrated in FIGURE 1). This damascene flow is preferably utilized when oxygen sensitive metal will be exposed (during the via etch process, preferably).

FIGURE 3 is a flow diagram illustrating the method of another embodiment of the instant invention. This method is preferably utilized in a dual damascene process flow where oxygen-sensitive (metal) structures are exposed (during the via etch process, preferably).

FIGUREs 4a-4h are cross-sectional views of a semiconductor device which is fabricated using the method of the instant invention (which is illustrated in FIGURE 3), incorporated into a dual damascene process flow where oxygen sensitive metal is exposed (during the via etch process, preferably).

FIGURE 5 is a flow diagram illustrating the method of another embodiment of the instant invention. This method of the instant invention is preferably utilized in a process flow where any exposed structures may or may not be oxygen-sensitive.

FIGUREs 6a-6d are cross-sectional views of a semiconductor device which is fabricated using the method of the instant invention (which is illustrated in FIGURE 5) incorporated into a non-damascene process, such as that used for Al metallization, for example.

## DETAILED DESCRIPTION OF THE DRAWINGS

While the methods of the instant invention are described with reference to FIGUREs 1-6, the methods of the instant invention can be applied to any type of device

structure (e.g. metal interconnects, metal lines, metal gates, or other conductive structures) and to any type of device (e.g. memory devices, logic devices, power devices, DSPs, or microprocessors). In addition, the method of the instant invention can be used to remove residue and/or photoresist from other device structures. Furthermore, while the methods of the instant invention, as described below, revolve around the use of hydrogen plasma, other plasmas may be used (such as a deuterium plasma, or other hydrogen- containing plasmas, such as  $\text{NH}_3$ ,  $\text{N}_2\text{H}_2$ ,  $\text{H}_2\text{S}$  and  $\text{CH}_4$ , and deuterated forms of these gases, for example).

The following method of one embodiment of the instant invention should preferably be used in a process flow where there are exposed portions of oxygen-sensitive conductive structures.

Referring to FIGURE 1 and FIGURE 2a, after providing substrate 202, isolation region 204 (which could be formed using LOCOS, field oxidation, or shallow trench isolation techniques), source/drain regions 208, gate dielectric 212, conductive gate structure 210, sidewall insulators 214, dielectric layer 216 (preferably comprised of BPSG, PSG, silicon oxide, oxide/nitride stack, TEOS, a low dielectric constant material, or any other interlevel dielectric material – in fact, regions 216 and 218 can be one layer), liner/barrier layer 220 (preferably comprised of Ti, TiN, or a Ti/TiN stack), conductor 222 (preferably comprised of aluminum, copper, copper-doped aluminum, or any other refractory metal), barrier layer 224 (preferably comprised of silicon nitride), dielectric layer 226 (preferably comprised of BPSG, PSG, TEOS, aerogel, xerogel, HSQ or any other low dielectric constant material), photoresist layer 230 is formed and patterned (step 102) over dielectric layer 226. Preferably, dielectric layer 226 is comprised of an oxide, an oxide/nitride stack, BPSG, PSG, TEOS, or a low dielectric constant material, such as aerogel, xerogel, HSQ, or a polymer. Opening 227 in photoresist 230 is preferably aligned with underlying metal structure 222, which may be surrounded by liner/barriers 220 and 224, as in the case of Cu metallization, for example, when the metal is oxygen sensitive. Preferably, conductive structure 222 is a

conductive line which is connected to other lines by interconnects and/or vias. Conductive structure 222 (for the damascene structure) is preferably comprised of copper or copper-doped aluminum (preferably on the order of 0.5 to 2.5 wt% of copper in aluminum). Liner/barriers 220 and 224 are comprised of titanium, titanium nitride, a Ti/TiN stack or other barrier-like material which adheres well to copper, aluminum and the interlevel dielectric material 218. Liner/barriers 220 and 224 may be comprised of the same material(s), but they do not have to be.

Referring to step 104 of FIGURE 1 and FIGURE 2b, an opening 228 is formed in dielectric 226 and liner/barrier layer 224 so as to expose at least a portion of conductor 222. Preferably, this is accomplished by subjecting the semiconductor wafer to  $CF_4$ ,  $CHF_3$ , or other fluorinated compound plasma environment.

Referring to steps 106 and 108 of FIGURE 1 and FIGURE 2c, in order to remove photoresist layer 230, passivate the exposed portion of conductor 222, and clean any polymer layers off of the exposed portions of conductor 222, the method of the instant invention is utilized. Using the method of the instant invention, photoresist 230 can be removed at the same time that the clean and passivation steps are performed. Preferably, in step 106 the photoresist is removed by subjecting the wafer to a photoresist removal step which uses a remote (or downstream) plasma and substantially no oxidizing chemical component. Hence, using the instant invention, the photoresist can be removed by subjecting it to a hydrogen-containing (with or without the addition of argon or nitrogen) or deuterium-containing photoresist removal process which uses a remote or downstream plasma. This may be followed by additional processing which includes subjecting the wafer to another hydrogen-containing etch process which preferably uses a remote or downstream plasma so as to remove any residue. Both of these process steps can be accomplished in Mattson, Applied Materials ASP, GaSonics International, or Fusion ashers or other similar processing tools. The hydrogen could be introduced with a forming gas such as  $N_2$  or Ar (where the hydrogen is 60 to 100% of the mixture) and/or deuterium may be used instead of hydrogen. If conductor 222 contains copper or other oxygen-sensitive material, and the

barrier layer 224 has been removed, it is important that step 108 not contain any appreciable amount of oxygen. However, step 106 may be accomplished in an oxygen-containing ambient (such as an ash step in an oxygen ambient with a downstream or remote plasma) so long as the barrier layer 224 has not yet been removed, or if the barrier layer 224 has been removed, an oxygen ash step may be done if it is followed by a hydrogen-based passivation step 108.

Preferably, the aforementioned process is performed in an ash tool which is provided with a plasma which is generated remotely from the wafer, such as with the Applied Materials ASP ash tool. The processing conditions are preferably around: 1 to 6 Torr (preferably around 2 to 4 Torr) ambient pressure; flow rates of 2500-4500 cm<sup>3</sup>/min; and an ambient temperature around 150 to 350 °C (preferably around 245 °C for the passivation step. For photoresist removal, the temperature may be 245 - 350 °C for achieving the most efficient photoresist removal rates.

In an alternative embodiment, the photoresist is removed during the hydrogen plasma step which utilizes a remotely generated plasma. Hence, steps 106 and 108 are combined in this embodiment. If conductor 222 contains copper or any other oxygen-sensitive compound, this unified step should, preferably, not contain an appreciable amount of oxygen.

In order to get a higher removal rate of the photoresist using the hydrogen or deuterium-containing remote plasma process, the energy of the plasma may be increased or the ambient temperature may be increased (preferably to around 245 °C to 350 °C; more preferably to around 245 to 250 °C ). While the higher temperature is preferable during the removal of the photoresist, it is not necessary during the subsequent clean step. However, the higher temperature is preferably used during the subsequent clean step (step 108) since it is inefficient to heat the process chamber and then cool it down for the subsequent step.

Referring to step 110 of FIGURE 1 and FIGURE 2d, liner/barrier 232 is preferably formed by chemical (CVD) or physical vapor deposition (PVD) on dielectric layer 226 and on the exposed portions of 222 (which should be free from any oxidation

and residue due to step 108). Preferably, liner/barrier 232 is comprised of a material which will act as a barrier, will adhere to dielectric layer 226, will act as an adhesion layer for conductor 234, and which is electrically conductive (more preferably liner/barrier 232 is comprised of Ti, TiN, or a Ti/TiN stack). Next, conductor 234 is formed, preferably by electroplating or PVD. Conductor 234 is preferably comprised of aluminum, copper doped aluminum, copper, or other conductor or refractory metal.

Referring to step 112 of FIGURE 1 and FIGURE 2e, conductor 234 is planarized so as to form interconnect 234. Preferably, the planarization is accomplished by chemical-mechanical polishing (CMP) or a blanket etch-back process. Liner/barrier 232 may remain intact (as is shown in FIGURE 2e), or the portions of liner/barrier 232 above dielectric 226 may be removed. This may be done during the planarization step or it may be done separately. Further processing can be performed using standard device processing techniques which would be obvious to one of ordinary skill in the art.

Referring to step 302 of FIGURE 3 and FIGURE 4a, after providing substrate 402, isolation region 404 (which could be formed using LOCOS, field oxidation, or shallow trench isolation techniques), source/drain regions 406, gate dielectric 408, conductive gate structure 412, sidewall insulators 410, dielectric layer 414 (preferably comprised of BPSG, PSG, silicon oxide, oxide/nitride stack, TEOS, a low dielectric constant material, or any other interlevel dielectric material – in fact, regions 414 and 416 can be one layer) liner/barrier layer 418 (preferably comprised of Ti, TiN, or a Ti/TiN stack), conductor 420 (preferably comprised of aluminum, copper, copper-doped aluminum, or any other refractory metal), barrier layer 422 (preferably comprised of silicon nitride), dielectric layer 424 (preferably comprised of BPSG, PSG, TEOS, aerogel, xerogel, HSQ or any other low dielectric constant material), photoresist layer 428 is formed and patterned over hardmask layer 426. Preferably, hardmask layer 426 is comprised of an oxide, an oxide/nitride stack, or silicon nitride (most preferably, it is comprised of a nitride).

Using the photoresist as a mask, hardmask 426 is etched so as to create opening 427 in the hardmask. Opening 427 is preferably aligned with underlying metal structure 420.

Referring to step 304 of FIGURE 3 and FIGURE 4b, photoresist 428 is removed. This may be accomplished by using a traditional oxygen ash step followed by a clean-up step, or the method of one embodiment of the instant invention can be used. Using the method of the instant invention, the wafer is subjected to a hydrogen-containing plasma so as to remove the photoresist and any residue. Preferably, the wafer temperature during this step is on the order of 150 to 350 °C (more preferably around 240 to 250 °C ). While a hydrogen plasma is preferable, one or more forming gases (such as N<sub>2</sub> or Ar) can be added and/or deuterium or other hydrogen-containing gases such as NH<sub>3</sub>, N<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>S, or CH<sub>4</sub>, or deuterated forms of these gases, for example, may be used instead of hydrogen. A subsequent clean-up step can be performed but it is not necessary.

Referring to step 306 of FIGURE 3 and FIGURE 4c, a dielectric material is formed on hardmask 426. Preferably, dielectric layer 430 is comprised of TEOS, BPSG, PSG, HSQ, or a low dielectric constant material, such as aerogel, xerogel, or a polymer (such as fluorinated parylene). Dielectric layer 430 is preferably either spun on or deposited using chemical vapor deposition (CVD).

Referring to step 308 of FIGURE 3 and FIGURE 4d, photoresist layer 432 is formed with a pattern. This is followed by an etch process to remove the exposed portions of dielectric layers 430 and 424, and create via opening 429. Preferably, this etch process is an anisotropic process, and, more preferably, it is performed using CHF<sub>3</sub>, CF<sub>4</sub> or other fluorinated hydrocarbon plasma chemistry. Referring to step 310 of FIGURE 3 and FIGURE 4e, an overetch process is performed to ensure completion of the dielectric etch. The barrier layer 422 is then removed (preferably using a fluorine-based plasma chemistry to remove Si<sub>3</sub>N<sub>4</sub>, for example) to expose the metal (Cu) layer 420.

Referring to step 312 of FIGURE 1 and FIGURE 4f, photoresist 432 is removed. This may be accomplished by using a traditional oxygen ash step followed by a clean-

up step, or the method of one embodiment of the instant invention can be used. The traditional oxygen ash step should not be performed if the exposed metal structure is comprised of a material that is oxygen sensitive (such as copper or copper doped aluminum). If a traditional photoresist removal step is performed, a subsequent clean-up step must be performed. The preferable clean-up step would include the method of the instant invention. More specifically, the wafer would be subjected to a hydrogen or deuterium containing plasma (which may also contain a forming gas such as  $N_2$  or Ar) at a wafer temperature around 150 to 350 °C. This clean-up step of the instant invention will remove any hydrocarbon residue left on metal structure 420 and will passivate metal structure 420.

Using the method of the instant invention to remove the photoresist, the wafer is subjected to a hydrogen-containing plasma so as to remove the photoresist and any residue resulting from the reaction of the anisotropic oxide etch chemistry with the photoresist layer. Preferably, the wafer temperature during this step is on the order of 150 to 350 °C (more preferably around 240 to 250 °C). While a hydrogen plasma is preferable, one or more forming gases (such as  $N_2$  or Ar) can be added and/or deuterium or other hydrogen-containing plasmas, such as  $NH_3$ ,  $N_2H_2$ ,  $H_2S$ , or  $CH_4$ , or deuterated forms of these gases, for example, may be used instead of hydrogen. A subsequent clean-up step can be performed but it is not necessary. The photoresist removal step may be followed by another hydrogen or deuterium step to further clean any residue left on exposed metal structure 420 and to passivate metal structure 420. This step is optional, since both of these advantages will be accomplished, to some extent, during the photoresist strip step of the aforementioned embodiment of the instant invention.

Referring to step 314 of FIGURE 3 and FIGURE 4g, a metal or other conductive material is formed over the liner 434. Liner layer 434 is preferably comprised of Ti, TiN, or a Ti/TiN stack. Preferably, metal layer 436 is comprised of aluminum, copper, copper-doped aluminum (preferably on the order of 0.5 to 5%; more preferably on the

order of 1 to 2%), or any other refractory metal. Metal layer 436 is preferably formed by electroplating, PVD or CVD or a combination thereof.

Referring to step 316 of FIGURE 3 and FIGURE 4h, metal structure 436 is planarized so as to form via and conductive line 438. Preferably, this planarization step is accomplished by CMP or a blanket etch-back step. The portion of liner/barrier 434 which is situated above dielectric 430 may be removed during this step, or it can be removed in a subsequent step.

While FIGURES 1-4h illustrate two different types of damascene process, the instant invention can be used on any type of damascene process or any other type of metallization process. One of ordinary skill in the art should be able to extrapolate the use of the instant invention in many different types of structure formation schemes based on his or her knowledge and the teachings in the instant specification.

The embodiment of the instant invention illustrated in FIGURES 5 and 6a-6d preferably utilizes a metal structure which is comprised of aluminum or aluminum doped with a smaller amount of copper (preferably on the order of 0.5 to 2 wt%; hence, a conductive structure which is not substantially sensitive to an oxygen ambient. While Cu doping of Al improves the electromigration resistance of the interconnect, pure copper structures and aluminum structures with greater than 5% copper doping are difficult to etch. The instant invention would work for such structures, in addition to pure Cu structures, if they could be etched.

Referring to step 502 of FIGURE 5 and FIGURE 6a, conductive stack 619 is formed above dielectric layers 616 and 614 (which may be formed in a single layer). Preferably, dielectric layers 614 and 616 are comprised of the same material which may include: BPSG, PSG, HSQ, silicon oxide, TEOS, or a low dielectric constant material (such as aerogel, xerogel, or a low-k polymer such as fluorinated parylene). An underlying structure may include: isolation region 604 (which may be comprised of a shallow trench isolation structure, a field oxide region, or a LOCOS region);



source/drain regions 606 formed in substrate 602, and a gate structure (comprised of conductive structure 612, sidewall insulators 610, and gate dielectric 608). Layers 614, 616 and the stack 619 can also be deposited on additional metal layers, while the different metal lines are connected by conducting vias. While FIGURES 6a-6d depict the first metal layer, this invention is applicable to any metal level.

Preferably, conductive stack 619 is comprised of titanium containing layer 618, titanium nitride containing layer 620, conductor 622, and an antireflective coating (ARC) 624. Preferably, conductor 622 is comprised of aluminum or copper-doped aluminum (where there is 0.5 to 2.5 wt% of copper), and ARC layer 624 is comprised of TiN, and optionally, an inorganic layer (such as  $\text{SiO}_x\text{N}_y$ ) or organic layer on top of the TiN layer. While layers 618, 620, and 624 are described herein to contain titanium or titanium nitride, these exact compositions are not necessary, they are merely the best choices for adhesion and barrier properties using present processing technologies. It should be obvious to one of ordinary skill in the art to use other combinations of materials.

Referring to step 504 of FIGURE 5 and FIGURE 6b, a patterned photoresist layer 626 is formed on ARC layer 624 by a sequence typically consisting of photoresist coating, lithographic patterning and developing, so as to provide a pattern for a subsequent conductor patterning step. Referring to step 506 of FIGURE 5 and FIGURE 6c, conductive stack 619 is patterned using photoresist layer 626 as a pattern mask. Preferably, step 506 is accomplished by a commercial metal etch reactor, such as an Applied Materials DPS reactor or a Lam Research Corporation TCP 9600 plasma reactor. In the case that an additional inorganic (such as  $\text{SiO}_x\text{N}_y$ ) or organic layer is used on top of the TiN ARC layer, this layer has to be opened prior to etching the conductive stack. Other than patterning conductive stack 619, the result of this step is to erode portions of photoresist layer 626 which forms a polymeric residue on conductors 625 and on the exposed portions of dielectric layer 616. The remaining photoresist and the residue must be removed.

Referring to steps 508 and 510 of FIGURE 5 and FIGURE 6d, photoresist 626 is removed next. Traditionally, photoresist 626 was removed by subjecting the wafer to an oxygen-containing ambient at an elevated temperature. In addition, an H<sub>2</sub>O-containing plasma has to be used to convert aluminum halide, which is the main etch byproduct and is the cause of aluminum corrosion if left on the etched surface, into volatile hydrogen halide. This may not be applicable in some processing chambers and it may cause problems if conductor 622 is comprised of an oxygen-sensitive material. In addition, if the traditional method is utilized, a subsequent clean-up step must be performed so as to remove any residue formed on the conductive structure. This clean-up step may utilize a solvent (wet) clean or it may utilize the (dry) clean-up step of the instant invention.

The method of the instant invention can be used to remove the photoresist, clean any residue, including aluminum halide, formed on the conductive structures and on the dielectric, and to passivate the conductive structure. Preferably, the method of the instant invention is comprised of subjecting the wafer to a hydrogen-containing or deuterium-containing plasma (preferably a remotely generated plasma) at an ambient temperature around 150 to 350 °C (more preferably around 200 to 260 °C – even more preferably around 240 to 250 °C). Alternatively, a multiple step ash and clean process may be used which includes both the H<sub>2</sub> or hydrogen- containing plasma and the conventional H<sub>2</sub>O/ O<sub>2</sub> plasma processes. In an alternative embodiment, the residue removal step of the instant invention is performed prior to the removal of the photoresist (where accomplished using the method of the instant invention or not).

While the embodiments of the instant invention are described above with regards to removing residue from metallic structures, the instant invention is equally applicable to removing residue from the sidewalls and other exposed portions of the dielectric layer. More specifically, residue, which is produced by the reaction of the photoresist with the fluorine-containing chemistry (used to etch the openings in the dielectric layers – preferably comprising an oxide) forms both on the underlying

metallic structure and on the exposed portions of the dielectric layer and is readily removed using any of the embodiments of the instant invention. Hence, when vias or openings are formed in the dielectric layers (which are covered with pattern photoresist), residues form on the sidewalls of the vias/openings in the dielectric layer and on the portion of the underlying conductor which is exposed by this newly formed via/opening in the dielectric layer. This residue can be removed by the methods of the instant invention.

Although specific embodiments of the present invention are herein described, they are not to be construed as limiting the scope of the invention. Many embodiments of the present invention will become apparent to those skilled in the art in light of the methodology of the specification. The scope of the invention is limited only by the claims appended.

**What we claim is:**

1. A method of fabricating an electronic device formed on a semiconductor wafer, said method comprising the steps of:

forming a layer of a first material over said substrate, said first material is oxygen-sensitive;

forming a photoresist layer over said layer of said first material;

patterning said layer of said first material;

removing said photoresist layer after patterning said layer of said first material;

and

subjecting said semiconductor wafer to a plasma which incorporates a gas which includes hydrogen or deuterium so as to remove residue from said first material.

2. The method of claim 1, wherein said step of removing said photoresist layer is performed by subjecting said semiconductor wafer to said plasma which incorporates a gas which includes hydrogen or deuterium.

3. The method of claim 1, wherein said step of removing said photoresist layer is performed by subjecting said semiconductor wafer to a higher temperature step which is conducted in a hydrogen ambient with a plasma impinging upon said semiconductor wafer.

4. The method of claim 3, wherein said higher temperature is around 245 °C.

5. The method of claim 1, wherein said gas additionally includes a forming gas.

6. The method of claim 5, wherein said forming gas is comprised of a gas consisting of: argon, nitrogen, and any other inert gas.

7. The method of claim 1, wherein said first material is comprised of a conductive material.

8. The method of claim 7, where said first material is selected from the group consisting of: copper, tantalum, titanium, titanium nitride, tungsten, tungsten nitride, aluminum, copper-doped aluminum, silver, gold, and any combination thereof.

9. A method of forming a conductive feature comprised of an oxygen-sensitive material over a semiconductor substrate for an electronic device, said method comprising the steps of:

forming a conductive layer over said semiconductor substrate, said conductive layer comprised of said oxygen-sensitive material;

forming a photoresist layer over said conductive layer, said photoresist having a pattern so as to expose portions of said conductive layer;

removing said exposed portions of said conductive layer so as to form said conductive structure; and

subjecting said semiconductor wafer to a plasma which incorporates a gas which includes hydrogen or deuterium.

10. The method of claim 9, wherein said oxygen-sensitive material is comprised of copper.

11. The method of claim 9, wherein said oxygen-sensitive material is comprised of tungsten.

12. The method of claim 9, wherein said oxygen-sensitive material is comprised of tungsten nitride.

13. The method of claim 9, wherein said oxygen-sensitive material is comprised of tantalum.
14. The method of claim 9, wherein said oxygen-sensitive material is comprised of titanium.
15. The method of claim 9, wherein said oxygen-sensitive material is comprised of TiN.
16. The method of claim 9, wherein said oxygen-sensitive material is comprised of aluminum.
17. The method of claim 9, wherein said oxygen-sensitive material is comprised of copper-doped aluminum.
18. The method of claim 9, wherein said oxygen-sensitive material is comprised of silver.
19. The method of claim 9, wherein said oxygen-sensitive material is comprised of gold.

20. A method of fabricating a conductive interconnect for providing an electrical connection between a first conductor and a second conductor for an electrical device formed in a semiconductor substrate, said method comprising the steps of:

forming a dielectric layer on said first conductor, said dielectric layer having at least one opening which exposes said first conductor;

forming a layer of an oxygen-sensitive material on said dielectric layer, said oxygen-sensitive material substantially filling said opening in said dielectric layer and for providing an electrical contact to said first conductor;

forming a photoresist layer on said oxygen-sensitive material, said photoresist layer having a pattern so as to expose portions of said oxygen-sensitive material;

removing said exposed portions of said oxygen-sensitive material on said dielectric material, said removal step causing a residue to be formed on exposed surfaces of the remaining portions of said oxygen-sensitive material; and

removing said photoresist layer by subjecting said photoresist layer with a hydrogen-containing gas incorporated into a plasma.

21. The method of claim 20, wherein said oxygen-sensitive material is comprised of a material selected from the group consisting of: copper, tungsten, tungsten nitride, tantalum, titanium, titanium nitride, aluminum, copper-doped aluminum, silver, gold, and any combination thereof.

22. The method of claim 20, further comprising the step of:

removing said residue by subjecting said residue to a fluorinated etchant.

23. The method of claim 21, wherein said fluorinated etchant is comprised of  $\text{CF}_4$ .

24. The method of claim 21, wherein said fluorinated etchant is comprised of  $\text{CHF}_3$ .

## ABSTRACT

Another embodiment of the instant invention is a method of fabricating a conductive interconnect for providing an electrical connection between a first conductor and a second conductor for an electrical device formed in a semiconductor substrate, the method comprising the steps of: forming a dielectric layer (layer 226 of FIGURE 2a) on the first conductor (conductor 222 of FIGURE 2a), the dielectric layer having at least one opening which exposes the first conductor; forming a layer of an oxygen-sensitive material (layer 234 of FIGURE 2d) on the dielectric layer, the oxygen-sensitive material substantially filling the opening in the dielectric layer and for providing an electrical contact to the first conductor; forming a photoresist layer on the oxygen-sensitive material, the photoresist layer having a pattern so as to expose portions of the oxygen-sensitive material; removing the exposed portions of the oxygen-sensitive material on the dielectric material, the removal step causing a residue to be formed on exposed surfaces of the remaining portions of the oxygen-sensitive material; and removing the photoresist layer by subjecting the photoresist layer with a hydrogen-containing gas incorporated into a plasma.



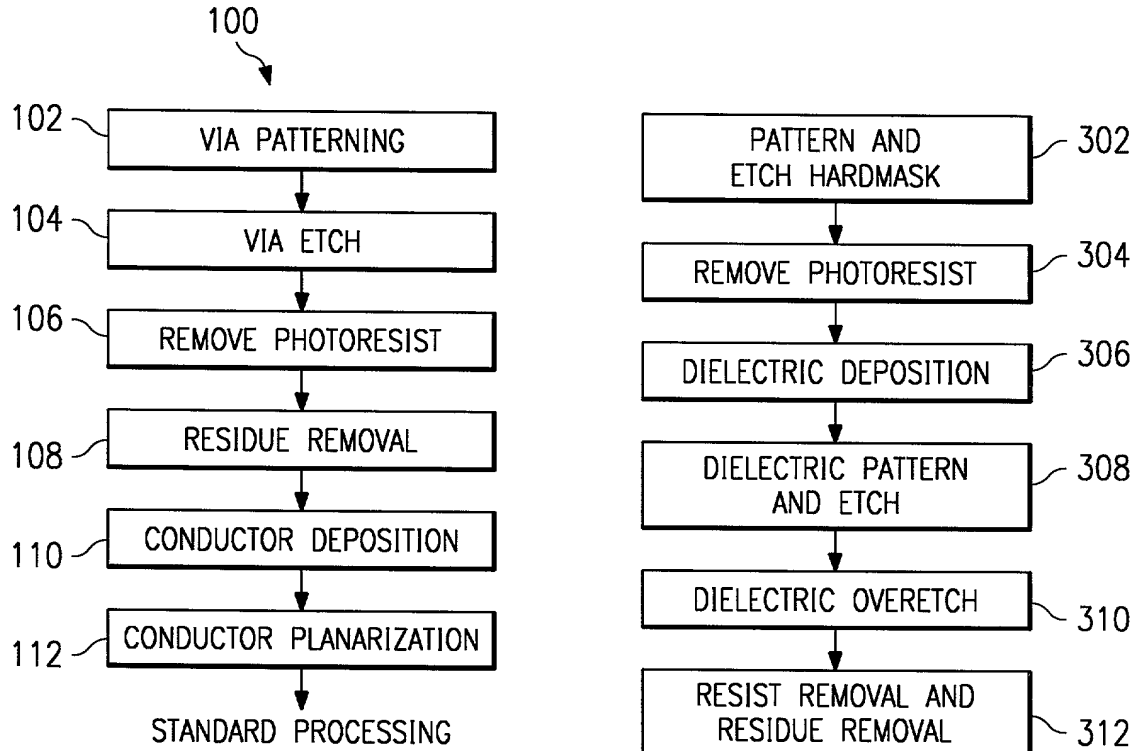


FIG. 1

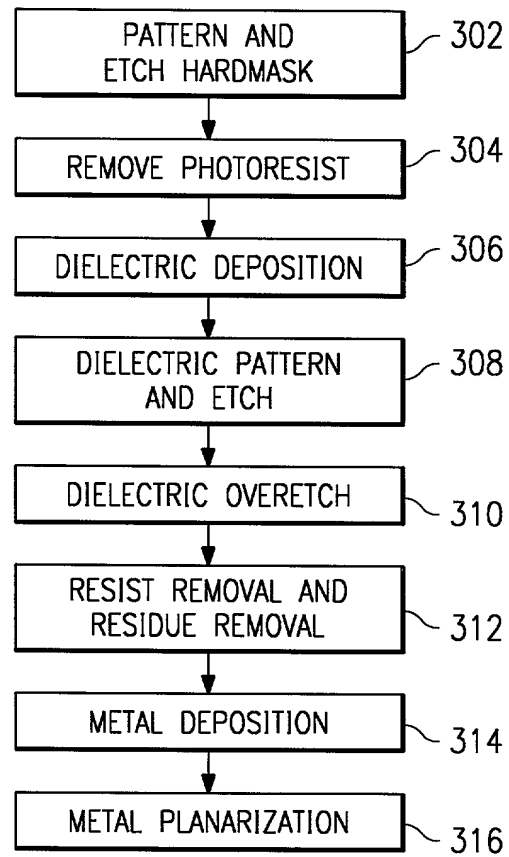


FIG. 3

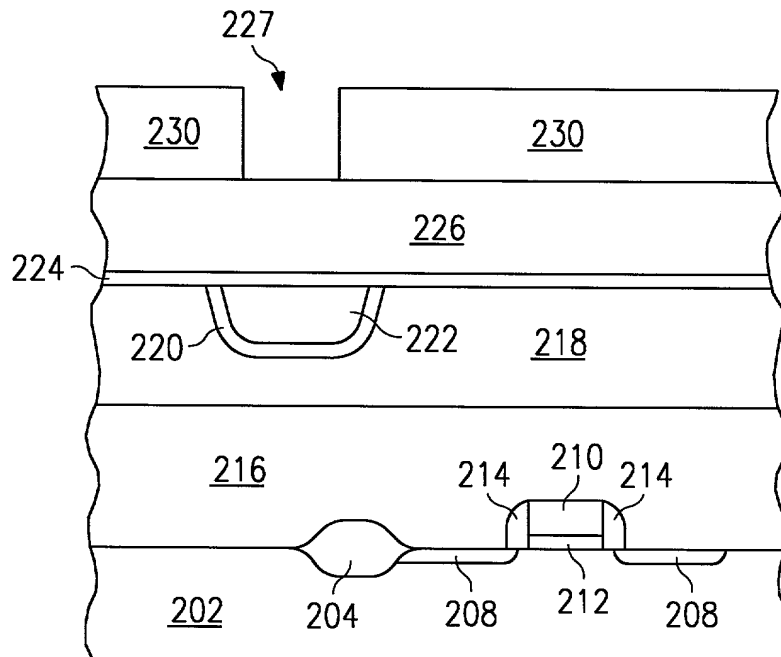


FIG. 2a

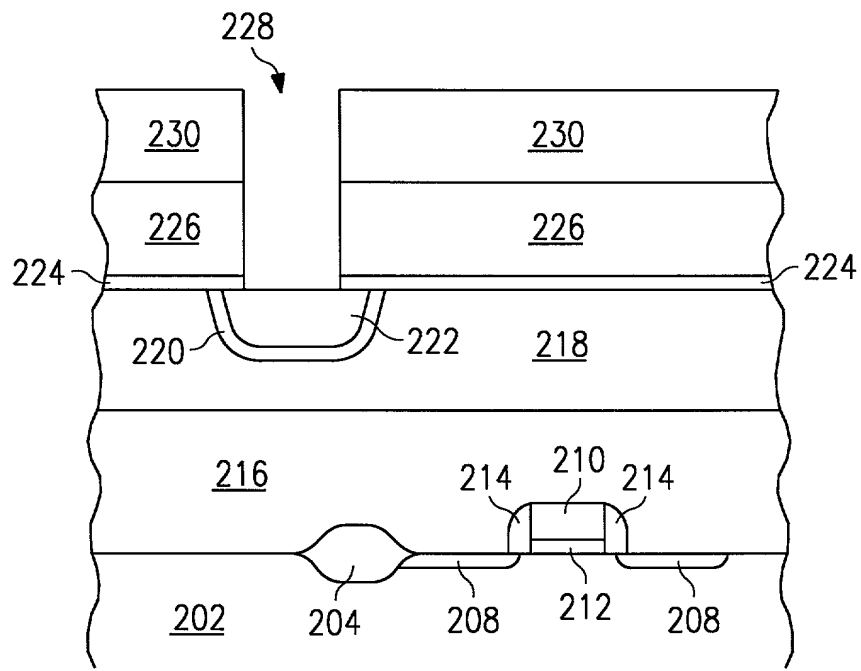


FIG. 2b

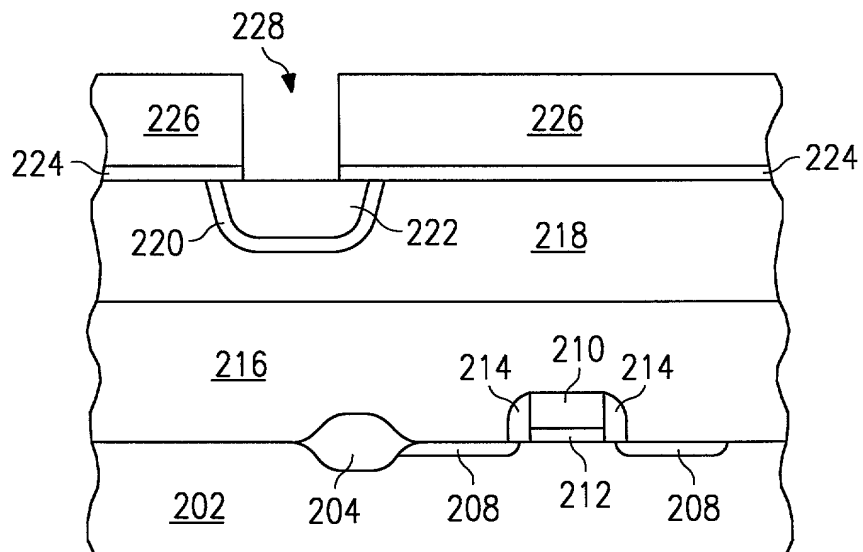


FIG. 2c

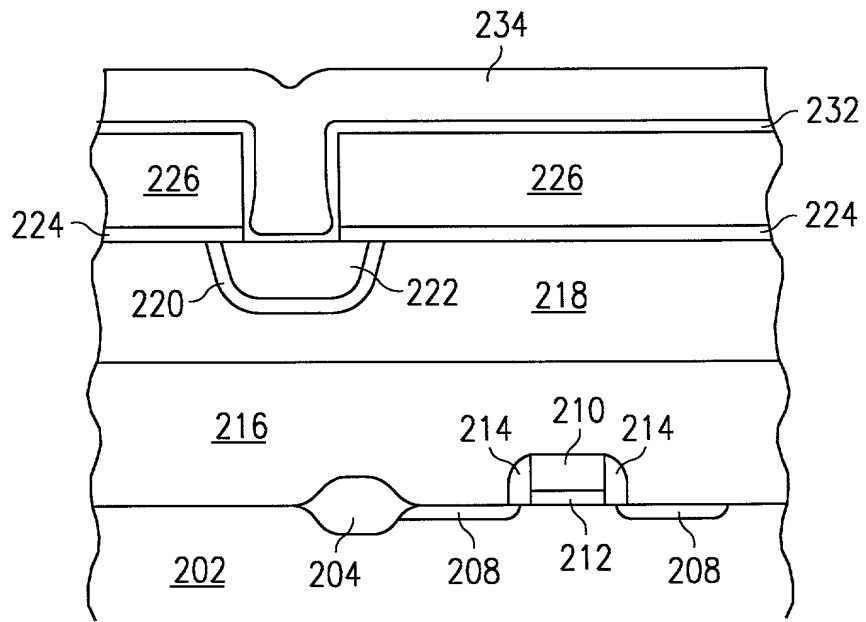


FIG. 2d

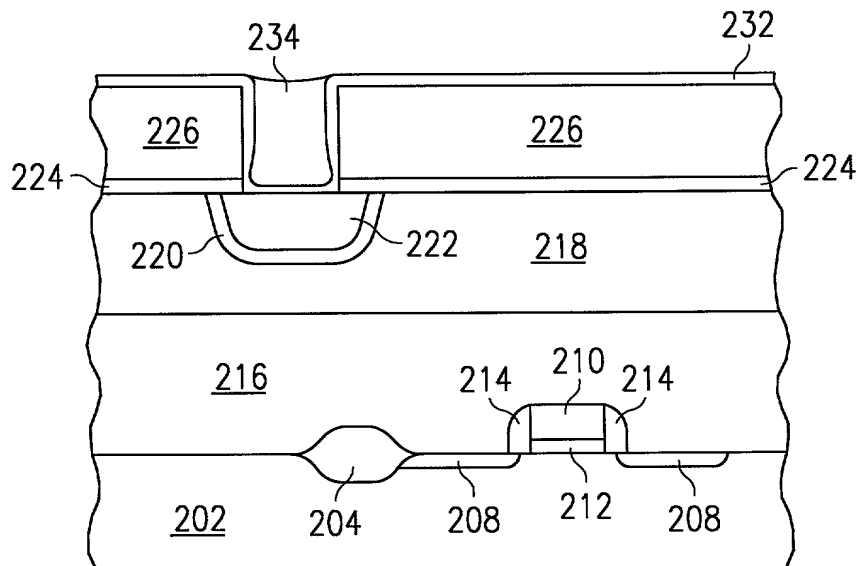


FIG. 2e

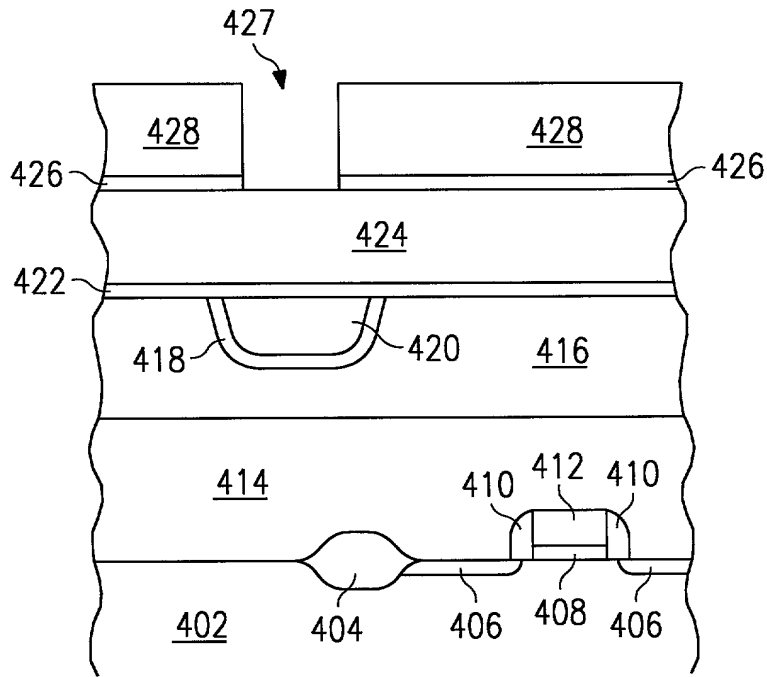


FIG. 4a

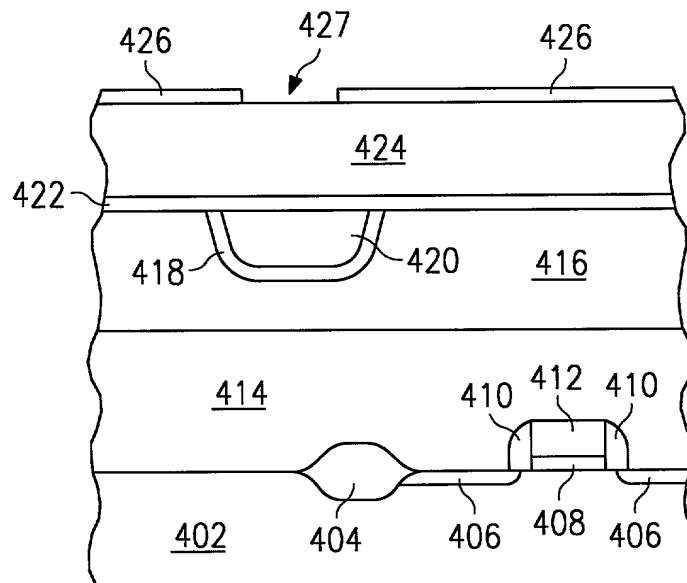


FIG. 4b

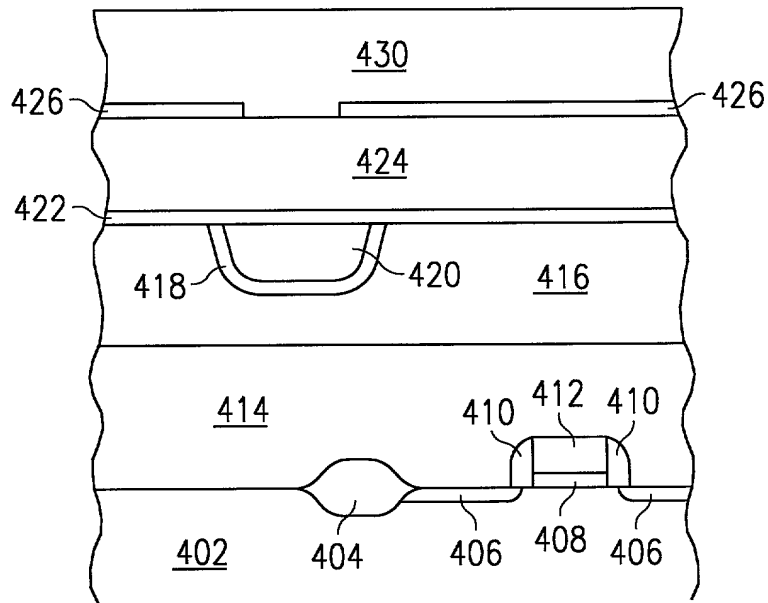


FIG. 4c

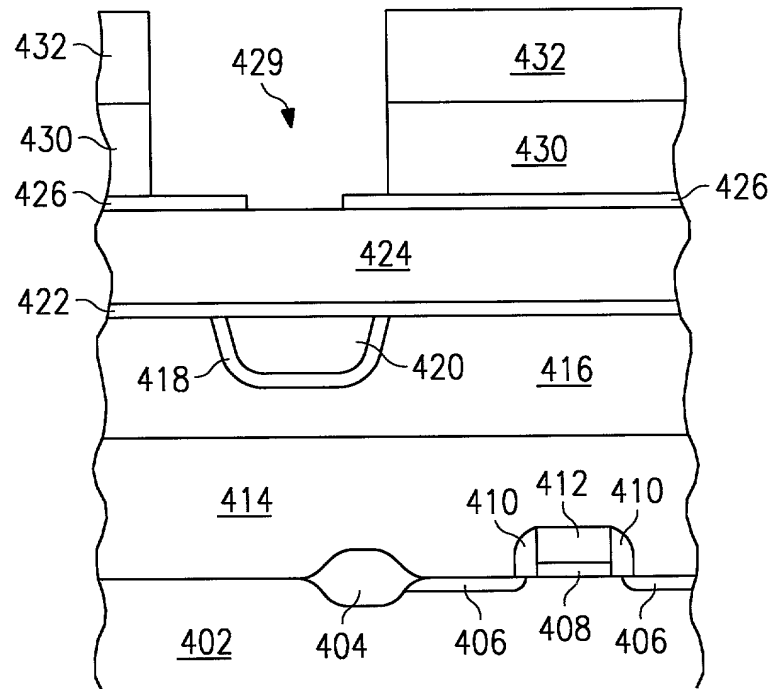


FIG. 4d

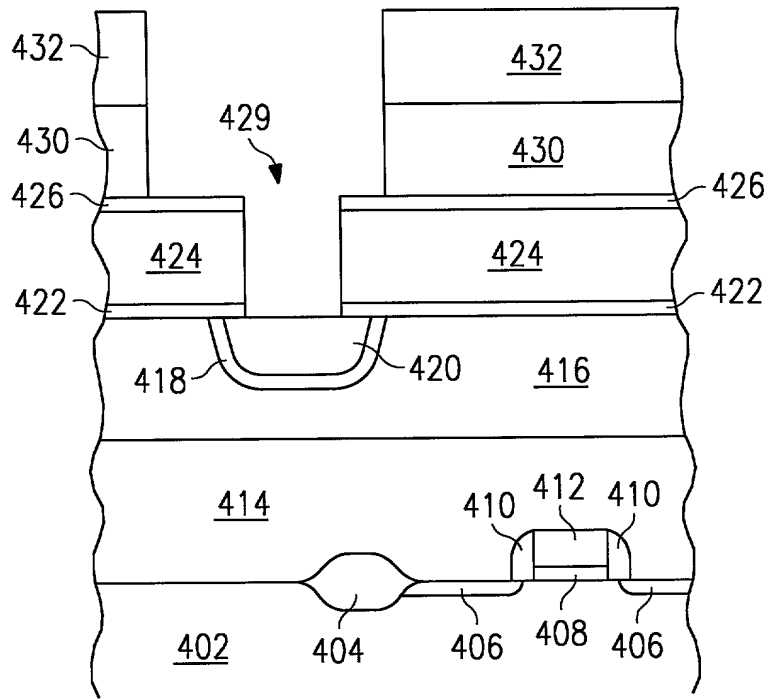


FIG. 4e

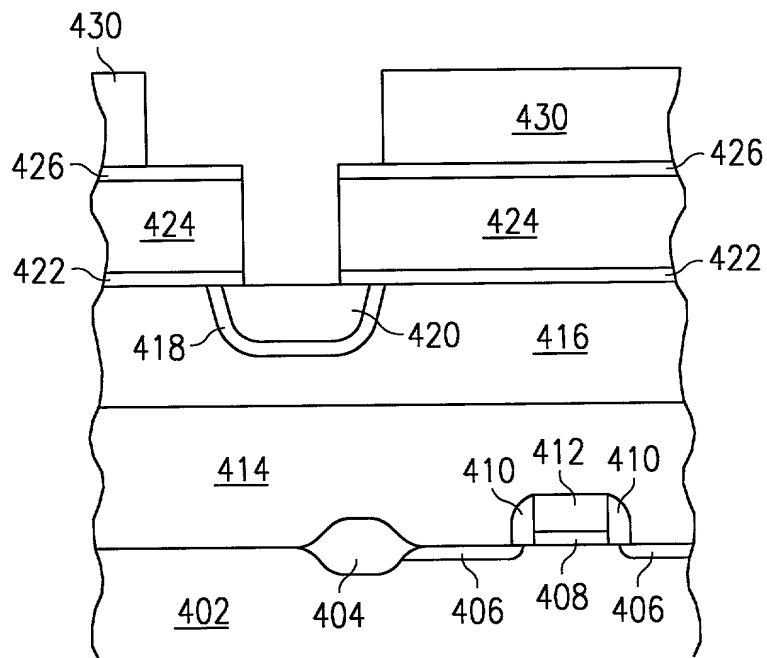


FIG. 4f

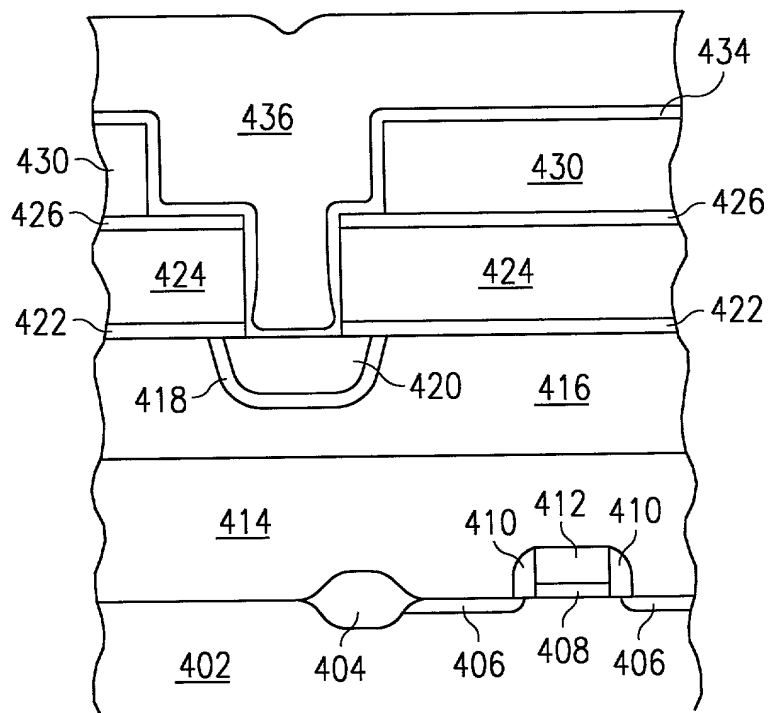


FIG. 4g

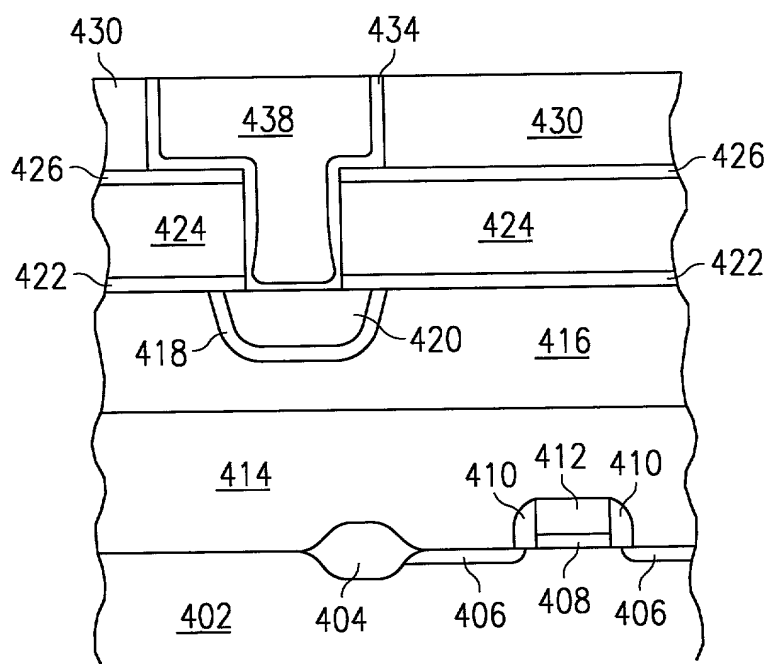


FIG. 4h

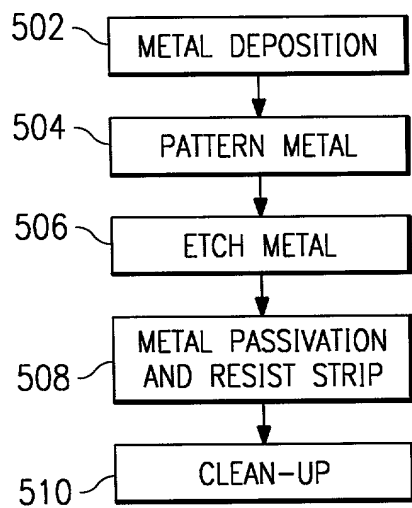


FIG. 5

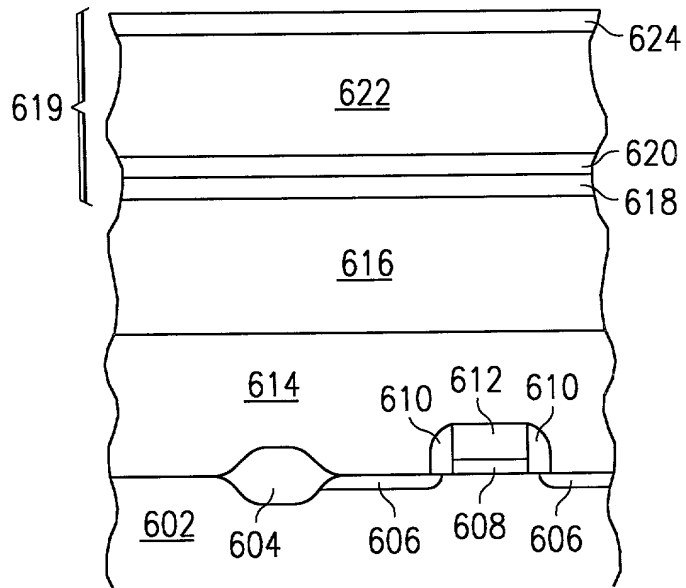


FIG. 6a

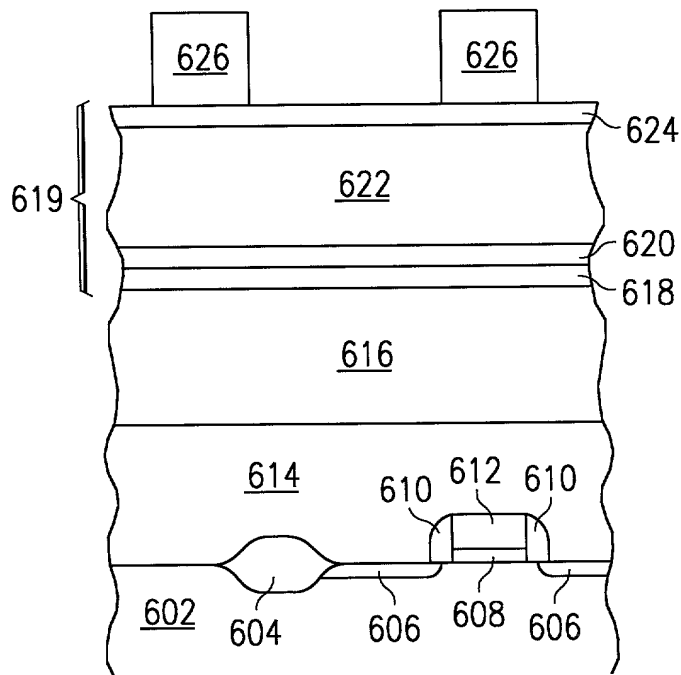


FIG. 6b



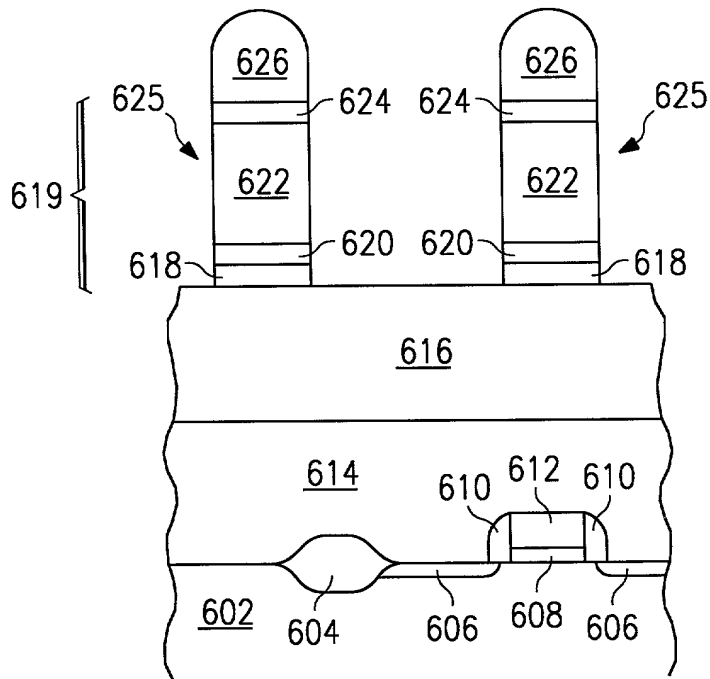


FIG. 6c

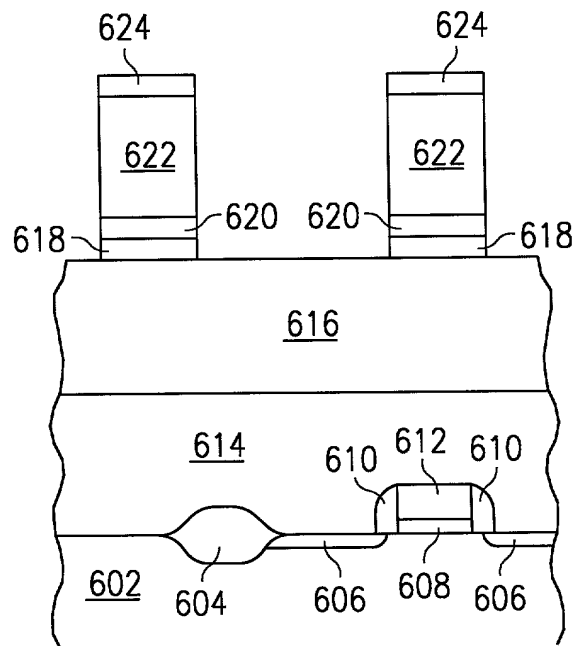




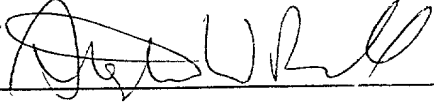
FIG. 6d

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**APPLICATION FOR UNITED STATES PATENT  
DECLARATION AND POWER OF ATTORNEY**

As a below named inventor, I declare that my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor if only one name is listed below, or an original, first and joint inventor if plural inventors are named below, of the subject matter which is claimed and for which a patent is sought on the invention entitled as set forth below, which is described in the attached specification; that I have reviewed and understand the contents of the specification, including the claims, as amended by any amendment specifically referred to in the oath or declaration; that no application for patent or inventor's certificate on this invention has been filed by me or my legal representatives or assigns in any country foreign to the United States of America; and that I acknowledge my duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56;

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

TITLE OF INVENTION:  HYDROGEN PLASMA PHOTORESIST STRIP AND POLYMERIC RESIDUE CLEANUP PROCESS FOR OXYGEN-SENSITIVE MATERIALS		
POWER OF ATTORNEY: I HEREBY APPOINT THE FOLLOWING ATTORNEYS TO PROSECUTE THIS APPLICATION AND TRANSACT ALL BUSINESS IN THE PATENT AND TRADEMARK OFFICE CONNECTED THEREWITH  Richard L. Donaldson, #25,673; William B. Kempler, #28,288; Jay M. Cantor, #19,906; Wade James Brady III, #32,080; Robby T. Holland, #33,304; Christopher L. Maginniss, #30,288; Alan K. Stewart, #35,373; Mark E. Courtney, #36,491; Rose A. Keagy, #35,095; Warren L. Franz, #28,716, Daniel W. Swayze, #34,478; Mark A. Valetti, #36,707.		
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COUNTRY OF CITIZENSHIP:  USA	COUNTRY OF CITIZENSHIP:  USA	COUNTRY OF CITIZENSHIP:  USA
SIGNATURE OF INVENTOR:  	SIGNATURE OF INVENTOR:  	SIGNATURE OF INVENTOR:  
DATE:  12-8-97	DATE:  12/5/97	DATE:  12/5/97